

NONLINEAR VISCOELASTIC MECHANICS OF CROSS-LINKED RUBBERS

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Abstract. *The paper develops a general theory for finite rubber viscoelasticity, and specifies it in the form, convenient for solving problems important for rubber, tire and space industries. Based on the quasi-linear approach of non-equilibrium thermodynamics, a general nonlinear theory has been developed for arbitrary non-isothermal deformations of viscoelastic solids. In this theory, the constitutive equations are presented as the sum of known equilibrium (rubber elastic) and non-equilibrium (liquid polymer viscoelastic) terms. These equations are then simplified using several modeling arguments. Stability constraints for the proposed constitutive equations are also discussed. It is shown that only strong ellipticity criteria are applicable for assessing stability of the equations governing viscoelastic solids.*

1 INTRODUCTION

Within the general rational mechanics¹, two types of continuum approaches to nonlinear constitutive equations (CE's) for viscoelastic solids have been suggested for applications. One is of the differential type (e.g. see^{2,3}), well developed for viscoelastic liquids on the basis of non-equilibrium thermodynamics. The other approach is the K-BKZ^{4,5} single-integral CE's. Both of them might be considered as complimentary in application to viscoelastic solids, and more precisely, to the *thermo-mechanical and relaxation properties of cross-linked rubbers*.

The effects of relaxation phenomena, which do not exist in pure elastic solids, enhance complexity of problems when polymers are considered. Hence, viscoelastic polymer solids demonstrate many nonlinear rheological effects, such as nonlinear creep and relaxation, hysteresis etc., which are not observed in other solids. Because of this, even geometrically simple problems that are analytically solvable for pure elastic solids have to be treated numerically in the viscoelastic case.

There are practical needs for developing a thermodynamically based approach to solid nonlinear viscoelasticity, which would be valid over a wide range of strains, strain rates (frequencies) and temperatures. It seems that this approach should combine (i) nonlinear multi-mode CE's of differential type generated by a part of relaxation spectrum with high relaxation times, and (ii) nonlinear single integral CE generated by that part of relaxation spectrum with low relaxation times. We suppose that both parts of the combined CE are almost independent. Part (i) governs the relatively slow motions of a continuum undergoing very large strains and obeying the WLF time-temperature superposition principle at relatively high temperatures. Part (ii) governs the fast (up to very fast) motions of continuum undergoing relatively small (even very small) strains and obeying a different time-temperature scaling that is valid for the glassy state. Thus the approach takes into account thermo-rheological complexity along with the high non-linearity of elastic and viscoelastic deformations, including compressibility effects. To make the approach reliable, the constraints of strong hyperbolicity and thermodynamic stability are imposed on the developed CE's. In this paper, only the first part of the above proposal, the part (i) of the CE's, is demonstrated. The second part (ii) will be displayed elsewhere.

In models of a differential type for viscoelastic solid (cross-linked) rubbers, the typical nonlinear pure elastic term should be included along with differential modes for different and well-separated relaxation times. The simple assumption is that this term is additive to the viscoelastic ones. In typical development^{6,7} of these models, only a nonlinear extension of the "standard" (three-parametric) linear viscoelastic solid model has been used. Also, the treatment of the dissipative term in the evolution equation for nonlinear Maxwell element in paper⁶ is not convincing, and the whole approach taken in the development of the evolution equation for this element in paper⁷ is questionable. An additional important question to ask of paper⁷, where both the pure gum elastomers and carbon black filled compounds were studied, is its treatment of Mullins hysteresis for carbon black filled rubbers as a pure relaxation effect. It is known, however, that this effect, being structurally reversible (i.e. thixotropic), takes several months at room temperature for a complete recovery⁸. The differential modeling has another importance:

one can establish the transformation of the CE from liquid to solid-like behavior via vulcanization using chemorheological modeling⁹. Surprisingly, this type of modeling was done first for filled elastomer compounds⁸.

Other nonlinear viscoelastic models of differential type have also been recently proposed in the literature, being based on pure continuum mechanics phenomenology. For example, several models have been developed (see paper¹⁰ and references there) that include nonlinear elements for modeling plasticity effects with a von-Mises type yield criterion. Also, in paper¹¹ the authors attempted to make a nonlinear extension of the linear 3-parametric "standard" model with two equivalent constructions of springs and dashpot. The two nonlinear models have been presented in an awkward form, based on the separation of the total viscoelastic strain into a product of elastic and inelastic components, with the use of the Second Law. Another approach¹², close in spirit to that elaborated here, has been recently introduced. There the author analyzed the viscoelastic solids in terms of a separated set of nonlinear Maxwell modes (with hidden tensor parameters), added to the equilibrium elastic mode. Although the equilibrium mode has been treated in a general and correct way, the evolution equations, as written, violate material objectivity, and the dissipation term was taken to be similar to the stress in the Maxwell mode (i.e. without strain induced anisotropy). The same defects in analyzing viscoelastic evolution equation in models for finitely deforming viscoelastic solids (extended from the three-parametric "standard" solid viscoelastic model) are observed in papers¹³⁻¹⁵. Stability constraints were not discussed in papers⁶⁻¹⁵.

The first step in a practical development of nonlinear models for viscoelastic solids using a multi-modal differential approach is elaboration of reliable methods for determining linear relaxation spectra. Since modern molecular models (e.g. see¹⁶⁻¹⁸) are still not reliable, the relaxation spectrum must be determined from experimental data. Because this problem is ill-posed, some mathematical methods have been elaborated. The Pade-Laplace method^{19,20}, developed for viscoelastic liquids, is the easiest and most reliable tool for effective discretization of relaxation spectra by a Prony series. When applying the Pade-Laplace method to a viscoelastic solid (e.g. for cross-linked elastomer) the true elastic component should be found first, via a preliminary experiment, and then removed from the Pade-Laplace procedure.

The structure of the paper is as follows. Adopting the thermodynamic approach^{2,3} developed for nonlinear liquid-like viscoelasticity, we initially develop a general nonlinear theory for elastic and viscoelastic nonlinear behavior of solids, with a single nonlinear relaxation mode. We simplify the developed theory and then extend this simplified format for the multi-mode case, along with a simplified fractioning of compressible and incompressible effects in nonlinear elasticity and viscoelasticity. We finish up by discussing the stability constraints imposed on the general theory, as well as on the simplified and extended models.

2 STATE VARIABLES AND FREE ENERGY

Here we will employ the general approach of irreversible thermodynamics discussed in various books (e.g. see²¹). We assume that in the simple case under study, the state variables for viscoelastic solid are: the temperature T , a measure of total strain, say, the Finger tensor \underline{B} , and a set of hidden variables that are taken to be symmetric, positive

definite, second-rank, non-dimensional tensors $\underline{\underline{b}}_k$. Each tensor $\underline{\underline{b}}_k$ is treated as the Finger elastic (recoverable) strain, with the capability of being independently measured. It is expected that a tensor $\underline{\underline{b}}_k$ is associated with the nonlinear k^{th} relaxation mechanism that, can hopefully can properly describe the (highly) nonlinear relaxation phenomena observed in cross-linked rubbers. In the following, we employ the Eulerian formulation for presenting our constitutive equations and, without loss of generality, use a Cartesian coordinate system.

To start off, we consider a single relaxation mechanism, whose elastic energy associated with a non-steady deformation is described by the tensor $\underline{\underline{b}}$. Being mostly interested in studies of isothermal deformation of isotropic viscoelastic solids, we introduce as a proper thermodynamic potential, the Helmholtz' free energy density F per mass unit, which depends on temperature T and the basic invariants of tensors $\underline{\underline{B}}$ and $\underline{\underline{b}}$. The crucial simplifying assumption underlying all of today approaches is that the free energy might be represented as a sum of two contributions, one from the equilibrium processes (with tensor $\underline{\underline{B}}$ as its parameter), and another from non-equilibrium processes (with tensor $\underline{\underline{b}}$ as its parameter):

$$F \approx F^0(T; I_1^B, I_2^B, I_3^B) + F^1(T; I_1, I_2, I_3). \quad (1)$$

Here I_j^B and I_j are respectively the basic invariants of tensors $\underline{\underline{B}}$ and $\underline{\underline{b}}$, defined as:

$$\begin{aligned} I_1^B &= \text{tr} \underline{\underline{B}}, \quad I_2^B = 1/2(I^2 - \text{tr} \underline{\underline{B}}^2), \quad I_3^B = \det \underline{\underline{B}}; \\ I_1 &= \text{tr} \underline{\underline{b}}, \quad I_2 = 1/2(I_1^2 - \text{tr} \underline{\underline{b}}^2), \quad I_3 = \det \underline{\underline{b}} \end{aligned} \quad (2)$$

Then the "thermodynamic" stress tensor $\underline{\underline{\sigma}}^T$ associated with the free energy F , is:

$$\underline{\underline{\sigma}}^T = \underline{\underline{\sigma}}_0 + \underline{\underline{\sigma}}_1, \quad (3)$$

wherein

$$\begin{aligned} \underline{\underline{\sigma}}_0 &= 2\rho \underline{\underline{B}} \cdot \partial F^0 / \partial \underline{\underline{B}} = 2\rho [F_1^0 \underline{\underline{B}} + F_2^0 (I_1^B \underline{\underline{B}} - \underline{\underline{B}}^2) + F_3^0 I_3^B \underline{\underline{\delta}}] \quad (F_j^0 = \partial F^0 / \partial I_j^B) \\ \underline{\underline{\sigma}}_1 &= 2\rho \underline{\underline{b}} \cdot \partial F^1 / \partial \underline{\underline{b}} = 2\rho [F_1^1 \underline{\underline{b}} + F_2^1 (I_1 \underline{\underline{b}} - \underline{\underline{b}}^2) + F_3^1 I_3 \underline{\underline{\delta}}]. \quad (F_j^1 = \partial F^1 / \partial I_j^1) \end{aligned} \quad (4)$$

In eqs.(3) and (4), ρ is the density, $\underline{\underline{\delta}}$ is the unit tensor, $\underline{\underline{\sigma}}_0$ and $\underline{\underline{\sigma}}_1$ are pure elastic (equilibrium) and viscoelastic (quasi-equilibrium) stresses, respectively. The only physical reason to use the suggested form in the second equation in (4) is the explicit assumption^{2,3} that polymeric liquids and solids always possess an "instantaneous" elastic limit, a quasi-equilibrium situation achieved on very fast (instantaneous) deformations,

where the temporary entanglements in macromolecules act like additional cross-links. Note that no incompressibility has been assumed here.

The well-known kinematical relation for the Finger total strain $\underline{\underline{B}}$,

$$\overset{\nabla}{\underline{\underline{B}}} \equiv \overset{0}{\underline{\underline{B}}} - \underline{\underline{B}} \cdot \underline{\underline{e}} - \underline{\underline{e}} \cdot \underline{\underline{B}} = \underline{\underline{0}}, \quad (5)$$

will be used in the following, where $\overset{\nabla}{\underline{\underline{B}}}$ and $\overset{0}{\underline{\underline{B}}}$ are upper convected and corotational (Jaumann) tensor time derivatives, and $\underline{\underline{e}}$ is the strain rate (or rate of deformation) tensor. The existence of a like kinematical (or *kinetic*) equation that governs the evolution of tensor $\underline{\underline{b}}$, the main goal of the following constitutive theory, has yet to be established.

3 ENTROPY PRODUCTION AND NONLINEAR NON-ISOTHERMAL RELAXATION PHENOMENA

The dissipative effects have been thoroughly analyzed for viscoelastic liquids^{2,3}. In viscoelastic solids, these effects are associated with their time dependent deformations. The Clausius-Duham expression for the entropy production P_s has the form:

$$TP_s = -\underline{q} \cdot \underline{\nabla} T + \text{tr}(\underline{\underline{\sigma}} \cdot \underline{\underline{e}}) - \rho dF/dt|_T \quad (\geq 0). \quad (6)$$

Using (4) and (5), we can rewrite eq.(6) as follows:

$$TP_s = -\underline{q} \cdot \underline{\nabla} T + \text{tr}[(\underline{\underline{\sigma}} - \underline{\underline{\sigma}}_0) \cdot \underline{\underline{e}}] - \text{tr}(\underline{\underline{\sigma}}_1 \cdot \underline{\underline{b}}^{-1} \cdot 1/2 \overset{0}{\underline{\underline{b}}}). \quad (7)$$

The next step is introducing the kinetic relation for tensor $\underline{\underline{b}}$, similar to the kinematical equation (5). This has been intensively discussed in Ref.³ and resulted in the definition of a "thermodynamic flux", the tensor $\underline{\underline{e}}_e$, such that

$$\overset{0}{\underline{\underline{b}}} - \underline{\underline{b}} \cdot \underline{\underline{e}}_e - \underline{\underline{e}}_e \cdot \underline{\underline{b}} = \underline{\underline{0}}. \quad (8)$$

Note that in the equilibrium limit, $\underline{\underline{b}} \rightarrow \underline{\underline{B}}$, $\underline{\underline{e}}_e \rightarrow \underline{\underline{e}}$, $\underline{\underline{\sigma}}_1 \rightarrow \underline{\underline{\sigma}}_0$, and eq.(8) coincides with eq.(5). Therefore it is convenient to introduce the pure non-equilibrium (dissipative) quantities, the stress $\underline{\underline{\sigma}}_p$ and strain rate $\underline{\underline{e}}_p$ that vanish in the equilibrium:

$$\underline{\underline{\sigma}}_p \equiv \underline{\underline{\sigma}} - \underline{\underline{\sigma}}^T = \underline{\underline{\sigma}} - \underline{\underline{\sigma}}_0 - \underline{\underline{\sigma}}_1; \quad \underline{\underline{e}}_p \equiv \underline{\underline{e}} - \underline{\underline{e}}_e. \quad (9)$$

Substituting the second relation in (9) into eq.(8) reduces the kinetic equation to the form:

$$\underline{\underline{b}} + \underline{\underline{b}} \cdot \underline{\underline{e}}_{\underline{\underline{p}}} + \underline{\underline{e}}_{\underline{\underline{p}}} \cdot \underline{\underline{b}} = 0. \quad (10)$$

Here the dissipative strain rate tensor $\underline{\underline{e}}_{\underline{\underline{p}}}$ has yet to be established, and is expressed as a function of temperature and the tensors $\underline{\underline{B}}$ and $\underline{\underline{b}}$.

Substituting also eqs.(9) into (10) into (7) finally yields:

$$TP_s = -\underline{\underline{q}} \cdot \underline{\underline{\nabla T}} + tr(\underline{\underline{\sigma}}_{\underline{\underline{p}}} \cdot \underline{\underline{e}}) + tr(\underline{\underline{\sigma}}_{\underline{\underline{1}}} \cdot \underline{\underline{e}}_{\underline{\underline{p}}}) (\geq 0). \quad (11)$$

The entropy production in eq.(43) is now presented as a typical bilinear form $\sum X_k \cdot Y_k$, where $\{X_k\} = \{\underline{\underline{\nabla T}}, \underline{\underline{\sigma}}_{\underline{\underline{p}}}, \underline{\underline{\sigma}}_{\underline{\underline{1}}}\}$ are the independent thermodynamic forces of different tensor dimensionalities, and conjugated to them are the quantities, $\{Y_k\} = \{\underline{\underline{q}}, \underline{\underline{e}}, \underline{\underline{e}}_{\underline{\underline{p}}}\}$, which are independent thermodynamic fluxes. Three independent dissipative sources are now clearly seen in equation (11). They are due to the non-isothermality (the first term in eq.(11)), and two contributions in mechanical dissipation in the system (the second and third terms in eq.(11)): (i) the mechanical dissipation produced by work of the irreversible stress $\underline{\underline{\sigma}}_{\underline{\underline{p}}}$ on the total strain rate $\underline{\underline{e}}$, and (ii) the mechanical dissipation produced by work of the viscoelastic stress $\underline{\underline{\sigma}}_{\underline{\underline{1}}}$ on the irreversible strain rate $\underline{\underline{e}}_{\underline{\underline{p}}}$.

Using the arguments of tensor dimensionality and Onsager symmetry of kinetic coefficients, we can write the CE's in the general quasi-linear form:

$$\underline{\underline{\sigma}}_{\underline{\underline{p}}} = \underline{\underline{M}}_1 : \underline{\underline{e}} - \underline{\underline{M}}_2 : \underline{\underline{\sigma}}_{\underline{\underline{1}}}; \quad \underline{\underline{e}}_{\underline{\underline{p}}} = \underline{\underline{M}}_2 : \underline{\underline{e}} + \underline{\underline{M}}_3 : \underline{\underline{\sigma}}_{\underline{\underline{1}}}; \quad \underline{\underline{M}}_k = \underline{\underline{M}}_k(T, \underline{\underline{B}}, \underline{\underline{b}}); \quad (12)$$

$$\underline{\underline{q}} = -\underline{\underline{\kappa}} \cdot \underline{\underline{\nabla T}}; \quad \underline{\underline{\kappa}} = \underline{\underline{\kappa}}(T, \underline{\underline{B}}, \underline{\underline{b}}) \quad (13)$$

Here the kinetic coefficients $\underline{\underline{M}}_k$ are tensors with rank of four, symmetric within the first and second pairs of indices, and symmetric by transposition between the first and second pairs of indices. Tensor $\underline{\underline{M}}_1$ has a dimensionality of viscosity, tensor $\underline{\underline{M}}_2$ is non-dimensional, and tensor $\underline{\underline{M}}_3$ has a dimensionality of reciprocal viscosity. The scalar products in eq.(12) mean, $(\underline{\underline{M}}_1 : \underline{\underline{e}})_{ij} \equiv M_{ijkl}^1 e_{lk}$, etc. The heat conductivity $\underline{\underline{\kappa}}$ is presented in eq.(13) as a second order symmetric tensor. The dependences of the kinetic tensors in eqs.(12) and (13) on the strain tensors $\underline{\underline{B}}$ and $\underline{\underline{b}}$ demonstrate the effect of strain induced anisotropy. Substituting eqs.(12) and (13) into eq.(11) presents the entropy production as the positively definite quadratic form:

$$TP_s = tr(\underline{\underline{\kappa}} \cdot \underline{\underline{\nabla T}} \underline{\underline{\nabla T}}) + TR(\underline{\underline{M}}_1 : \underline{\underline{e}} \underline{\underline{e}}) + TR(\underline{\underline{M}}_3 : \underline{\underline{\sigma}}_{\underline{\underline{1}}} \underline{\underline{\sigma}}_{\underline{\underline{1}}}) (\geq 0). \quad (14)$$

Due to eq.(14) the second rank tensor $\underline{\underline{\kappa}}$ and the two rank of four kinetic tensors $\underline{\underline{M}}_1$ and $\underline{\underline{M}}_3$ are positively definite. Eq.(14) imposes no thermodynamic constraint on the kinetic

coefficient \mathbf{M}_2 from eq.(12). The complicated general structure of the rank-four kinetic tensors was explicitly exposed in Ref.²². The general structure of the heat conductivity tensor $\underline{\kappa}(T, \underline{B}, \underline{c})$, also quite complicated, can be readily established using the representation theorems¹ (p.35). Equations (10), (12) and (13) present the closed set of CE's for non-isothermal, finite, solid, compressible viscoelasticity.

Introducing the heat capacity c_d under constant tensors \underline{B} and \underline{b} as $c_d = \partial U / \partial T \big|_{\underline{B}, \underline{b}}$, reduces the balance of internal energy U to the common heat equation:

$$\rho c_d dT / dt = \nabla \cdot \underline{\kappa} \cdot \nabla T + tr(\underline{\sigma} \cdot \underline{e}). \quad (15)$$

In the case of rubber (entropic) elasticity, when $U = U(T)$, the heat capacity c_d is the function of only temperature.

The above general phenomenological relations include in the consideration the Kelvin-Voight stress that denies the commonly known "instantaneous" elastic response that has been well documented in experiments. Therefore in the following, the only admissible type of solid viscoelasticity, the Maxwell type with instantaneous response, will be analyzed. This considerably simplifies the above CE's to the form:

$$\underline{\sigma} = \underline{\sigma}^T = \underline{\sigma}_0 + \underline{\sigma}_1 \quad (\mathbf{M}_1 = \mathbf{0}, \mathbf{M}_2 = \mathbf{0}); \quad \underline{e}_p = \mathbf{M}(T, \underline{B}, \underline{b}) : \underline{\sigma}_1 \quad (\mathbf{M} \equiv \mathbf{M}_3). \quad (16)$$

Here the expressions for $\underline{\sigma}_0$ and $\underline{\sigma}_1$ are given in eq.(4).

4 COMPRESSIBILITY EFFECTS

Although the above general theory includes the compressibility effects, it is convenient to expose them explicitly using the density as a new variable. We analyze initially the compressibility effects in single-mode viscoelastic approach with instantaneous elasticity.

In the equilibrium (pure elastic) case, the free energy is represented in the form: $F = F^e(T; I_1^B, I_2^B, I_3^B)$, the stress tensor is given by the second formula in (4), with the kinematical relation (5). Additionally, there are two well-known equations for mass conservation:

$$I_3^B = (\rho_0 / \rho)^2, \quad \partial_t \rho + \nabla \cdot (\rho \underline{u}) = 0 \quad \text{or} \quad d \ln \rho / dt = -tr \underline{e}. \quad (17)$$

Here \underline{u} is the velocity vector. Note that the second relation in eq.(17) is easily derived from the first one and the kinematical equation (5). Using the first relation in eq.(17) we now introduce instead of tensor \underline{B} , its "incompressible" part $\hat{\underline{B}}$ and density ρ ,

$$\hat{\underline{B}} = (I_3^B)^{-1/3} \underline{B} \equiv (\rho / \rho_0)^{2/3} \underline{B}, \quad (18)$$

with corresponding invariants \hat{I}_j^B of tensor $\hat{\underline{B}}$ as:

$$\hat{I}_1^B \equiv \text{tr} \hat{\underline{\underline{B}}} = (\rho / \rho_0)^{2/3} I_1^B, \quad \hat{I}_2^B = \text{tr} \hat{\underline{\underline{B}}}^{-1} = (\rho / \rho_0)^{4/3} I_2^B, \quad \hat{I}_3^B = 1. \quad (19)$$

Using eq.(19) the free energy F^0 , can be expressed via the density ρ and new invariants \hat{I}_1^B and \hat{I}_2^B as: $F^0(T, I_1^B, I_2^B, I_3^B) = \hat{F}^0(T, \rho, \hat{I}_1^B, \hat{I}_2^B)$, with the representation of the stress tensor as:

$$\underline{\underline{\sigma}}^0 = -\rho^2 \hat{F}_\rho^0 \underline{\underline{\delta}} + 2\rho [\hat{F}_1^0 (\hat{\underline{\underline{B}}} - 1/3 \hat{I}_1^B \underline{\underline{\delta}}) - \hat{F}_2^0 (\hat{\underline{\underline{B}}}^{-1} - 1/3 \hat{I}_2^B \underline{\underline{\delta}})]. \quad (20)$$

Eq.(20) has been derived by Truesdell²³. The first term there represents the equilibrium thermodynamic pressure, and the second, deviatoric term, demonstrates the effects of isochoric (“shearing”) deformations. Finally, using eqs.(17) and (18) reduces eq.(5) to the “incompressible” form:

$$\overset{\nabla}{\underline{\underline{B}}} \equiv \overset{0}{\underline{\underline{B}}} - \hat{\underline{\underline{B}}} \cdot \hat{\underline{\underline{e}}} - \hat{\underline{\underline{e}}} \cdot \hat{\underline{\underline{B}}} = \underline{\underline{0}}; \quad \hat{\underline{\underline{e}}} \equiv \underline{\underline{e}} - 1/3 \delta \text{tr} \underline{\underline{e}} = \underline{\underline{e}} - 1/3 \delta \rho^{-1} d\rho / dt. \quad (21)$$

The above derivation is repeated in the non-equilibrium, viscoelastic case, starting with the introduction of a new irreversible (“density-like”) variable ρ^i as: $\rho^i / \rho_0 = I_3^{-1/2}$, and leading to the similar formulae,

$$\hat{\underline{\underline{b}}} = (I_3)^{-1/3} \underline{\underline{b}} \equiv (\rho^i / \rho_0)^{2/3} \underline{\underline{b}}, \quad (18a)$$

$$\hat{I}_1 \equiv \text{tr} \hat{\underline{\underline{b}}} = (\rho^i / \rho_0)^{2/3} I_1, \quad \hat{I}_2 = \text{tr} \hat{\underline{\underline{b}}}^{-1} = (\rho^i / \rho_0)^{4/3} I_2, \quad \hat{I}_3 = 1. \quad (19a)$$

Using eqs.(18a), (19a) reduces the evolution equation (10) to the following:

$$\overset{0}{\underline{\underline{b}}} - \hat{\underline{\underline{b}}} \cdot \hat{\underline{\underline{e}}} - \hat{\underline{\underline{e}}} \cdot \hat{\underline{\underline{b}}} + \hat{\underline{\underline{b}}} \cdot \hat{\underline{\underline{e}}}_p + \hat{\underline{\underline{e}}}_p \cdot \hat{\underline{\underline{b}}} = \underline{\underline{0}}; \quad d \ln \rho^i / dt - \text{tr} \underline{\underline{e}}_p = d \ln \rho / dt = -\text{tr} \underline{\underline{e}}. \quad (22)$$

Here $\hat{\underline{\underline{e}}}$ and $\hat{\underline{\underline{e}}}_p$ are the *deviators* of the tensors $\underline{\underline{e}}$ and $\underline{\underline{e}}_p$, respectively.

Finally, using for the non-equilibrium part of free energy F^1 the presentation $F^1(T, I_1, I_2, I_3) = \hat{F}^1(T, \rho^i, \hat{I}_1, \hat{I}_2)$, similar to that for the equilibrium part F^0 , results in the formulae for the complete stress tensor in the irreversible case:

$$\underline{\underline{\sigma}} = -p^T \underline{\underline{\delta}} + \hat{\underline{\underline{\sigma}}}; \quad p^T = p_0 + p_1; \quad \hat{\underline{\underline{\sigma}}} = \hat{\underline{\underline{\sigma}}}_0 + \hat{\underline{\underline{\sigma}}}_1. \quad (23)$$

$$p_0 = \rho^2 \partial \hat{F}^0 / \partial \rho, \quad p_1 = \rho \rho^i \partial \hat{F}^1 / \partial \rho^i; \quad (24)$$

$$\hat{\underline{\underline{\sigma}}}_0 = 2\rho [\hat{F}_1^0 (\hat{\underline{\underline{B}}} - 1/3 \hat{I}_1^B \underline{\underline{\delta}}) - \hat{F}_2^0 (\hat{\underline{\underline{B}}}^{-1} - 1/3 \hat{I}_2^B \underline{\underline{\delta}})]. \quad (25)$$

$$\hat{\underline{\underline{\sigma}}}_1 = 2\rho [\hat{F}_1^1 (\hat{\underline{\underline{b}}} - 1/3 \hat{I}_1 \underline{\underline{\delta}}) - \hat{F}_2^1 (\hat{\underline{\underline{b}}}^{-1} - 1/3 \hat{I}_2 \underline{\underline{\delta}})]. \quad (26)$$

Here p^T is the thermodynamic pressure due to compressibility of the viscoelastic solid, with equilibrium p_0 and non-equilibrium p_1 components; $\underline{\hat{\sigma}}$ is the thermodynamic stress deviator consisting of two, equilibrium $\underline{\hat{\sigma}}_0$ and non-equilibrium $\underline{\hat{\sigma}}_1$, deviator components.

5 SIMPLIFICATIONS AND MULTI-MODAL GENERALIZATIONS

Although only the theory with instantaneous elastic reply is considered in Section 3 and below, it still requires more simplifications to be useful in practice. We now consider several modeling arguments and corresponding steps introducing more simplicity in the theory.

(i) The first step directed toward simplifying CE's has already been made in eq.(1), which in fact is *decoupling the free energy into a sum of equilibrium and quasi-equilibrium parts*. Although there are some fundamental questions regarding the validity of this decoupling, it has been successfully used in many non-equilibrium theories.

(ii) In spirit of the point (i), it is also assumed that *it is possible to decouple the irreversible effects from the equilibrium response*. It practically means that the kinetic tensor \mathbf{M} in eq.(16) depends on the temperature and non-equilibrium elastic tensor \underline{b} .

This immediately reduces the evolution equation for tensor \underline{b} to the form:

$$\underline{\dot{b}} + \varphi(T, \underline{b}) = \underline{0}. \quad (10a)$$

This form has successfully been used in the thermodynamic theories^{2,3} for viscoelastic liquids. Here in (10a) $\varphi(T, \underline{b})$ is an isotropic tensor function of tensor \underline{b} , whose properties and specifications have been established in Refs.^{2,3}

(iii) *Decoupling the bulk and shearing properties*. This can be justified in the case of large strains with relatively very small bulk deformations, which is the case of rubber elasticity.

(iiia) *Decoupling of the bulk and shearing thermodynamic properties*. For the free energy this means the additivity:

$$F = F^0(T; I_j^B) + F^1(T; I_j^1) = F_b^0(T; \rho) + F_{sh}^0(T; \hat{I}_1^B, \hat{I}_2^B) + (\rho^i / \rho_0) F_b^1(T; \rho^i) + F_{sh}^1(T; \hat{I}_1, \hat{I}_2). \quad (27)$$

The stress tensor due to eq.(27) is therefore represented as:

$$\underline{\sigma} = \underline{\sigma}_0(T, \underline{B}) + \underline{\sigma}_k(T, \underline{b}_k) = -[p_0(T, \rho) + p_k(T, \rho^i)] \underline{\delta} + \underline{\hat{\sigma}}_0(T, \underline{\hat{B}}) + \underline{\hat{\sigma}}_k(T, \underline{\hat{b}}_k) \quad (28)$$

(iiib) *Decoupling of the bulk and shearing relaxation properties*. Eq.(22) with the use of simplification in (ii) (see eq.(10a)) can be represented as:

$$d \ln \rho^i / dt + [\alpha(\rho^i) / \theta_b^1(T)] (\rho^i)^2 \partial \hat{F}_b^1 / \partial \rho^i(T, \rho^i) = d \ln \rho / dt \quad (29)$$

$$\underline{\hat{b}} - \underline{\hat{b}} \cdot \underline{\hat{e}} - \underline{\hat{e}} \cdot \underline{\hat{b}} + 1/2 [\beta(\hat{I}_1, \hat{I}_2) / \theta_1(T)] \cdot [\underline{\hat{b}}^2 - 1/3 (\hat{I}_1 - \hat{I}_2) \underline{\hat{b}} - \underline{\delta}] = \underline{0}. \quad (30)$$

Equations (27)-(30) impose the full decoupling of bulk and shear viscoelastic evolution equations. Due to the Second Law, the functions $\alpha(\rho^i)$ and $\beta(\hat{I}_1, \hat{I}_2)$ are positive. They go to the unity in the equilibrium limit, when $\rho^i \rightarrow \rho_0$, $\hat{I}_1 \rightarrow \hat{I}_2 \rightarrow 3$, and represent the strain scaling factors for corresponding relaxation times, which are similar in concept to the “material clocks” of the K-BKZ theory. The dissipative term in eq.(29) is written in general form, whereas in eq.(30) it has been presented in the form proposed and tested for polymer fluids and a gum rubbers³. The temperature dependent parameters $\theta_b^1(T)$ and $\theta_1(T)$ are the bulk and shear relaxation times, which occur in linear viscoelasticity.

(iv) *Simplified models for the heat conductivity tensor $\underline{\kappa}$ in (13) can be suggested when the tensor depends only on the equilibrium strain \underline{B} , i.e. $\underline{\kappa} = \underline{\kappa}(T, \underline{B})$. This dependence predicts that after unloading the heat conductivity is isotropic. Therefore the crucial test is measuring heat conductivity in a retardation experiment (i.e. after unloading).*

In the multi-mode generalization of CE's for nonlinear solid-like viscoelasticity, we adopt all of the modeling simplifications discussed above for a single relaxation mode. We additionally advance the assumption that both the bulk and shearing relaxation times are well separated:

$$\theta_k(T) \gg \theta_{k+1}(T); \quad \theta_k^b(T) \gg \theta_{k+1}^b(T). \quad (31)$$

Inequalities (31) which hold for viscoelastic liquids³ give the opportunity to consider overall nonlinear properties as the sum of nonlinear viscoelastic properties for independent relaxation modes, where the free energy and stress (both bulk and shear components) are the sums of these for nonlinear relaxation modes. Additionally, the evolution equations of type (29), (30) also hold. For cross-linked rubbers, the fore mentioned closed set of nonlinear constitutive equations of differential type has the nice feature: they can model the properties of rubber-like materials in both the flow and solid regions with changing parameters during cure reaction, when keeping the same mathematical structure of equations, except for the equilibrium part.

Additionally, some scaling approaches, like well-known *time-temperature scaling* of WLF type, could apply to both shear and bulk relaxations. Furthermore, the *deformation scaling*²⁴ developed for viscoelastic liquids, if applicable, could significantly simplify numerical computations for viscoelastic solids, too.

6 STABILITY CONSTRAINTS FOR CONSTITUTIVE EQUATIONS FOR VISCOELASTIC SOLIDS

The formulation of field equations for viscoelastic solids should obey some stability constraints. These constraints take into account the most fundamental properties of CE's, related to the Second Law of thermodynamics, propagating various fast waves, and the fundamental condition providing the continuity for a solution of a problem along the time axis. *Unlike CE's for viscoelastic liquids, in the case of viscoelastic solids, these constraints are related only to the Hadamard stability (or the strong ellipticity, or the strong hyperbolicity for wave propagating, or well posedness).*

In the case of finite elasticity, the general (necessary and sufficient) condition of *strong ellipticity* is:

$$\mathbf{A} = A_{ijmn}(\underline{\underline{B}}) x_i y_j x_m y_n > 0. \quad (32)$$

The rank of four tensor A_{ijmn} is defined for isotropic solids as:

$$A_{ijmn}(\underline{\underline{B}}) = \frac{\partial \sigma_{ij}}{\partial h_{mn}} = \frac{\partial}{\partial h_{mn}} \left(\rho \frac{\partial F}{\partial h_{ij}} \right) = 4 B_{mk} \frac{\partial}{\partial B_{kn}} \left(\rho B_{il} \frac{\partial F}{\partial B_{lj}} \right). \quad (33)$$

Here \underline{h} is the Hencky strain measure. Condition (32) of strong ellipticity means the positive definiteness of the tensor A_{ijmn} considered in terms of a bi-quadratic form. It was reduced in both incompressible²⁵ and compressible^{26,27} cases to a set of algebraic inequalities imposed on the first and second free energy derivatives taken with respect to three basic invariants I_k . In the case of the linear stability analysis of disturbances imposed on arbitrary, nonlinear, and generally time dependent stress-strain deformation field, condition (32) of strong ellipticity coincides with the condition of *strong hyperbolicity*:

$$\rho \Omega^2 \bar{v}_i \bar{v}_i = A_{ijmn}(\underline{\underline{B}}) \bar{v}_i k_j \bar{v}_m k_n > 0. \quad (34)$$

Here $\Omega = \omega - \underline{k} \cdot \underline{v}$ is the frequency oscillations in the disturbance wave with a Doppler's shift of the basic velocity field $\underline{v} = \underline{v}(x, t)$ being taken into account, where k_i and \bar{v}_j are respectively the components of the wave vector and the vector amplitude of the velocity disturbances. In the limit $\omega \rightarrow \infty, k \rightarrow \infty$ one can consider a monochromatic plane wave of disturbances as being restricted to a local analysis of stability. It has been proved (e.g. see²⁸) that when a system is described by the quasi-linear set of PDE, the linear stability analysis coincides with more general method of characteristics. Positive definiteness of the form (34) means the possibility to continue in the positive direction of time axis, at any time instant, any solution of the equations for finite elasticity. If this is impossible, the characteristics are turned back, and near a turning point, their derivatives approach to infinity. Thus, Hadamard instability is a typical ill posedness accompanying by the blow-up instability. In the general case of compressibility, all possible types of waves of disturbances are allowed, including longitudinal waves. However, when an elastic material is treated as incompressible, i.e. $\rho = \text{const}$, the longitudinal waves of disturbances are forbidden. Thus because of the incompressibility condition, the wave and the velocity amplitude vectors are orthogonal: $k_j \bar{v}_j = 0$.

When analyzing static stability, where infinitesimal (symmetric) strain disturbances $\underline{\underline{\varepsilon}}$ are imposed on a given finite elastic strain $\underline{\underline{B}}_0$, so that $\underline{\underline{B}} = \underline{\underline{B}}_0 + \underline{\underline{\varepsilon}}$, one obtains (instead of the strong ellipticity condition of eq.(32)), a *thermodynamic stability* condition:

$$\mathbf{A}_T = A_{ijmn}(\underline{\underline{B}})\varepsilon_{ij}\varepsilon_{mn} > 0 \quad (35)$$

Although the fourth-rank tensor A_{ijmn} is once again defined by eq.(33), it is easy to see that the thermodynamic condition of stability (35) is only a *necessary condition* for strong ellipticity (32).

The necessary and sufficient conditions for strong ellipticity are too complex and awkward to be applied to every newly proposed CE. Therefore, several attempts have been undertaken to find non-trivial, yet simple enough, *sufficient conditions* of strong ellipticity.

Renardy²⁹ proved that the CE's for incompressible elastic and viscoelastic solids are strongly elliptic, if the strain energy function $F = F(T, I_1, I_2)$, which here depends only on two basic invariants, I_1 and I_2 , can be represented as monotonically increasing and convex function of $\sqrt{I_1}$ and $\sqrt{I_2}$. More complicated sufficient conditions for strong ellipticity in compressible case have been recently derived in paper³⁰.

7 REMARKS OF SPECIFICATION OF FUNCTIONS AND PARAMETERS

This Section briefly surveys the various literature specifications of mechanical properties for rubber-like materials. More detailed description will be given in presentation and elsewhere.

It has been documented^{31,32} that the *bulk properties* of cross-linked rubbers are well described by the van der Waals equation, where stability constraints can also be imposed. Although the most popular for numerical applications is the Mooney-Rivlin potential, its descriptive ability of *shearing properties* for the rubber materials is rather limited³³.

To the authors' knowledge, the widest range in description of various experimental data for the cross-linked rubbers has been achieved using the Blatz-Sharda-Tschoegl (BST) potential³⁴, which operates with the generalized strain measure $\underline{\underline{B}}^n$. However, their model does not lend itself to computational efficiency, since these problems can be effectively treated only in the principal axes of tensor $\underline{\underline{B}}$. The stability constraints for this potential are unknown, mostly because of the generalized strain measure involved.

Another elastic potential that has been recently proposed and well tested for viscoelastic liquids³⁵ can also be used for crosslinked rubbers. This potential is a combination of the Mooney-Rivlin and Knowles³⁶ potentials, widely used for calculations of large deformations of elastic solids. Using the Renardy sufficient condition of strong ellipticity, some sufficient stability criteria for this potential might be able to be established.

Several recent attempts were also made to propose expressions for elastic potentials for very large deformations of elastic solids (e.g., see^{37,38}), related to the finite extensibility of elastomer chains. These approaches used the inverse Langevin function, which is too complicated for solving complex problems. The easiest semi-empirical way to include this effect into consideration was proposed by Gent³⁹, who was unaware that the same approach has been proposed for viscoelastic liquids (see Ref.⁵) utilizing Warren's approximation of the inverse Langevin function ("Warren spring"⁴⁰). This type of potential, depending only on I_1 , might describe well enough very large elastic

deformations. These usually occur in uniaxial extension or in situations close to that, which can be met in complex deformations with high-level concentrations of stresses. However, at relatively low strains, predictions of this potential are in contradiction with experimental data³³, which clearly show the dependence of elastic stress on the second invariant I_2 . This means that in low and intermediate regions of elastic strains, the potential³⁵ might be more preferable. It is possible to combine the potentials proposed in papers^{35,36} for describing the large range of elastic deformations presented in rubbers.

To describe the *non-equilibrium nonlinear viscoelastic properties* of crosslinked rubbers one has to specify the elastic potentials for the tensors $\underline{b}_{=k}$ and scaling factors presented in the evolution equations. The elastic potential that describes bulk non-equilibrium properties could be taken, once again, in the van der Waals form^{31,32}, and a potential for shear properties could be taken in the form used in Ref.³⁵ for viscoelastic liquids. The function β , which describes the dissipative properties in shear evolution equations (36), could also be extracted from Ref.³⁵, where it has been applied to viscoelastic liquids. The function $a(\rho_k^i)$, which describes the dissipative properties in bulk evolution equations (35), has yet to be determined via experimental studies and/or theoretical modeling.

Finally, the effects of *stress induced anisotropy in thermal conductivity* found in papers^{42,43} for uniaxial extension, could be easily generalized. This will be demonstrated in the presentation.

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